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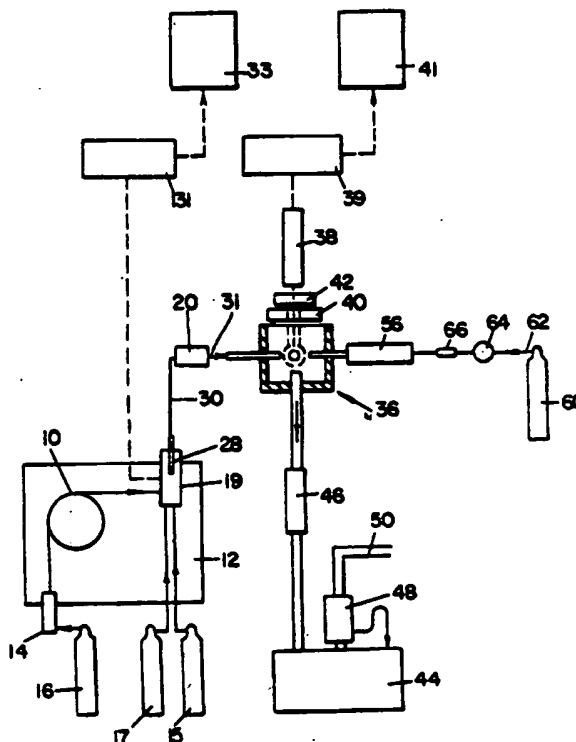
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(21) International Application Number: PCT/US95/01899 (22) International Filing Date: 10 February 1995 (10.02.95) (30) Priority Data: 08/195,148 10 February 1994 (10.02.94) US (71) Applicant: SIEVERS INSTRUMENTS, INC. [US/US]; Suite H1, 2500 Central Avenue, Boulder, CO 80301 (US). (72) Inventors: GODEC, Richard, D.; 1038 Spencer, Longmont, CO 80501 (US). SHEARER, Randall, L.; 912 Palisade Court, Louisville, CO 80027 (US). (74) Agents: BEATON, Glenn, K. et al.; Beaton & Folsom, P.C., Suite 403, 4582 South Ulster Street Parkway, Denver, CO 80237 (US).		(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.

(54) Title: APPARATUS FOR SIMULTANEOUS MEASUREMENT OF SULFUR AND NON-SULFUR CONTAINING COMPOUNDS

(57) Abstract

A method and apparatus for simultaneously measuring sulfur and non-sulfur compounds in a sample. The non-sulfur compounds are measured by introducing the sample into a flame-type detector (12) such as a flame ionization detector or flame photometric detector. A portion of the exhaust gases are then collected and transferred to a burner for conversion of sulfur compounds to sulfur monoxide. The sulfur monoxide is then reacted with ozone to produce excited state sulfur dioxide which is allowed to chemiluminescence.



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**APPARATUS FOR SIMULTANEOUS MEASUREMENT
OF SULFUR AND NON-SULFUR
CONTAINING COMPOUNDS**

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FIELD OF THE INVENTION

This invention relates to a process and apparatus for simultaneously detecting and quantifying trace amounts of sulfur and non-sulfur containing compounds using, in part, a sulfur chemiluminescence detector.

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BACKGROUND OF THE INVENTION

Various processes have been devised for the measurement of the chemical components of a complex mixture separated by gas, liquid or supercritical fluid carriers, and for the measurement of the composition of gas, liquid and supercritical fluid streams or the gases evolved upon heating a solid matrix. Representative of such processes are detection by changes in physical properties of the streams, including changes in the refractive index and thermal conductivity. Another detection scheme is based on the measurement of electrical currents induced by the formation of ionic species during combustion of a stream (flame ionization or "FID"). Irradiation of a stream using electromagnetic radiation and radioactive sources or changes in the absorption of electromagnetic radiation by components of a stream are also employed.

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In general, these processes allow detectors that can be classified as either "general" or "universal" detectors. These detectors produce a response for all of the chemical constituents contained in a carrier stream (except for the eluent or carrier itself). Selective detectors, on the other hand, respond to specific chemical constituents based on one or more elements within each compound detected and/or unique physical or chemical properties of the components. Selective

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detection is often required when the chemical components of interest are present at low concentrations, together with much high concentrations of other chemicals in the stream.

5 Detection systems can be further classified as being non-destructive detectors, in which the chemical composition of the stream is not altered by the measurement process, or destructive detectors, in which
10 the sample is destroyed or chemically altered as a result of the measurement process. Generally, to use a destructive detector, such as a flame ionization detector, in combination with a selective detector, it is
15 necessary to split the sample stream prior to measurement of the chemical constituents by the respective detectors. Difficulties in controlling the amount of the sample
stream which flows into the different detectors using stream splitting has severely limited the utility of this technique.

20 In chromatographic analysis, the identity of a chemical compound is determined based on the "retention time" of the compound in a chromatographic system. The amount of the compound is determined based on the detector response. Typically, several analyses are
25 performed using standard solutions of the test compound at different concentrations. Based on this information, a calibration curve is constructed by comparing the detector response (e.g. peak area) to the amount of
30 injected compound. For both "universal" and "selective" detectors, retention time as well as response of a given chemical compound relative to a "standard" compound provide information regarding the identity of the chemical.

35 Once response factors for a wide range of chemical compounds are known, it is possible to determine the concentrations of different compounds based solely on

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their retention times and detection response without the need for constructing calibration curves for each individual component. For example, relative response factors using a flame ionization detector are available for a large number of hydrocarbons and other chemical compounds found in petroleum and petrochemical samples, thus greatly simplifying quantifications of these complex samples. Comparison of the relative response factors for compounds on two or more different detectors provides even more information regarding the identity of a particular chemical compound, since fundamentally different measurement techniques are employed.

An important class of selective detectors are devices for the selective measurement of sulfur-containing compounds. When present as impurities at low concentrations, sulfur-containing compounds are detrimental to a wide range of chemical processes. In consumer products, trace levels of sulfur-containing compounds can impart objectionable taste and odor to the products. In petrochemical applications, trace sulfur contaminants can rapidly poison costly catalysts. For these reasons, numerous processes and apparatus have been developed for the measurement of low concentrations of sulfur-containing compounds in sample streams.

Representative of such processes is that disclosed in West German Patent No. 1,133,918 to H. Drägerwerk and B. Dräger for the flame photometric detector (FPD). Sulfur-containing compounds are oxidized in a hydrogen/air flame to form diatomic sulfur S_2 in an electronically excited state. Emission of light from this species can be measured using a photomultiplier tube or similar light detection device equipped with an optical filter to eliminate the light emitted from other species in the flame. Through the use of different optical filters, the FPD can also be used for the

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measurement of phosphorus-containing compounds based on the emission of light from electronically excited phosphorus dioxide (PO_2) formed in the hydrogen/air flame. Compounds that do not contain sulfur or phosphorus cannot be measured using the FPD. However, compounds that do not contain sulfur or phosphorous can result in a decrease or "quenching" of the detector response for sulfur and phosphorous-containing compounds. S.O. Farwell and C.J. Barinaga, Sulfur-Selective Detection with the FPD: Current Enigmas, Practical Usage, and Future Directions, 24 Journal of Chromatographic Science, 483 (1986).

The reactive sulfur and phosphorus species generated in the FPD flame are short-lived and therefore require that the light measurement device be located in close proximity to the flame. This basic design requirement has precluded the simultaneous operation of the FPD with other "universal" detection systems, such as the flame ionization detector. Of course, there is no such thing as a truly universal detector. For example, the flame ionization detector responds sensitively to nearly all organic compounds (excluding formaldehyde and formic acid) but not to inorganic compounds (e.g., O_2 , N_2 , Ar, CO_2 , H_2S , COS, etc.).

Another example of selective detection of sulfur-containing compounds is that disclosed in U.S. Patents Nos. 4,678,756 and 4,352,779 of R.E. Parks. According to this process, a sample is passed through a furnace containing a metal oxide catalyst to convert sulfur-containing compounds to sulfur dioxide. The sulfur dioxide is then passed through a second furnace, where the sample is mixed with hydrogen gas to facilitate the conversion of sulfur dioxide to hydrogen sulfide. The effluent of the second furnace is then directed into a reaction cell where the hydrogen sulfide is mixed with

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ozone and the resultant chemiluminescence is measured by means of a photomultiplier tube. In the system described by Parks, non-sulfur-containing compounds cannot be measured, since the expected products from the oxidation furnace (carbon dioxide and/or carbon monoxide) and from the reduction furnace (methane) either do not undergo an ozone-induced chemiluminescent reaction, or the light emitted from such reactions is eliminated through the use of optical filters.

Numerous other patents and publications may be found which disclose other approaches to the selective detection of sulfur-containing compounds. Gaffney and co-workers have described a technique for the measurement of reduced sulfur compounds (e.g., hydrogen sulfide, methanethiol, dimethyl sulfide, etc.) based on reactions of the sulfur-containing compounds with ozone to form electronically excited sulfur dioxide (SO_2^*) which then emits radiation in the 200 nm to 400 nm region of the spectrum. J.S. Gaffney, D.F. Spandau, T.J. Kelly, R.L. Tauner, Gas Chromatographic Detection of Reduced Sulfur Compounds Using Ozone Chemiluminescence, 347 Journal of Chromatography 121 (1985). This detection system does not permit measurement of all sulfur-containing compounds (e.g., sulfur dioxide) and suffers from interferences from non-sulfur-containing compounds such as olefins.

Birks and co-workers have described a sulfur selective detector based on fluorine-induced chemiluminescence. J.K. Nelson, R.H. Getty, J.W. Birks, Fluorine Induced Chemiluminescence Detector for Reduced Sulfur Compounds, 55 Analytical Chemistry 1767 (1983). Reduced organic sulfur-containing compounds (e.g. mercaptans, sulfides, disulfides, etc.) react with molecular fluorine to form vibrationally excited hydrogen fluoride and other electronically and vibrati nally excited species which emit radiation in the red and n ar

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infrared region of the spectrum. Inorganic sulfur-containing compounds (e.g., H_2S , SO_2 , etc.) do not undergo fluorine-induced chemiluminescence, while many non-sulfur-containing compounds, such as olefins and aromatic hydrocarbons, do react and interfere in the measurement of sulfur compounds.

Other workers have described a detection system based on the reaction of sulfur-containing compounds with chlorine dioxide. These reactions result in the formation of electronically excited diatomic sulfur, which emits radiation in the visible region of the spectrum (250 to 450 nm).

None of these previously reported systems for the measurement of sulfur-containing compounds permit the simultaneous measurement of non-sulfur-containing compounds, without the need for splitting the sample to a second "universal" detector system.

Halstead and Thrush have described the chemiluminescent reaction of sulfur monoxide with ozone. The Kinetics of Elementary Reactions Involving the Oxides of Sulphur III. The Chemiluminescent Reaction Between Sulphur Monoxide and Ozone, C.J. Halstead, B.A. Thrush, 295 Proceedings of the Royal Society, London, 380 (1966). Sulfur monoxide, produced from sulfur dioxide using a microwave discharge, was reacted with ozone. One of the reaction products was identified as electronically excited sulfur dioxide. The emission spectrum from this species was recorded and found to extend from 280 to 420 nm, with maximum emission at 350 nm.

Previous studies have shown that sulfur monoxide is one of the species formed in the combustion of sulfur compounds in a flame. Sulfur Chemistry in Flames, C.H. Muller, et al., in 17th International Combustion Symposium, pp. 867-879 (1989) and Experimental and Numerical Studies of Sulfur Chemistry in $H_2/O_2/SO_2$

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Flames, M.R. Zachariah, O.I. Smith 69, Combustion and Flame 125 (1987). Under the typical operating conditions of the FPD, sulfur monoxide is present at about 10 times the levels of diatomic sulfur.

5 On the basis of these observations, Benner and Stedman reported the development of a "Universal Sulfur Detector" (USD) based on the formation of sulfur monoxide in a hydrogen/air flame and subsequent detection of SO based on a chemiluminescent reaction with ozone. R.L. Benner, D.H. Stedman, Universal Sulfer Detection by Chemiluminescence, 60 Analytical Chemistry 1268 (1989).
10 The original embodiment of the USD was a continuous monitor for the measurement of the total concentration of sulfur-containing compounds in ambient air. The USD is also described in the parent U.S. patent application
15 Serial No. 07/275,980. In this design, the air stream containing the sulfur compounds is mixed with an excess of hydrogen in a quartz burner assembly equipped with an external ignition source. A quartz sampling probe is
20 used to collect sulfur monoxide and other products from the flame for transfer to a modified nitric oxide/ozone chemiluminescence detector.

 This detection system was found to provide greater sensitivity for the measurement of sulfur-containing compounds than existing sulfur-selective
25 detectors and did not suffer interferences in the measurement of sulfur species due to the presence of higher concentrations of non-sulfur species such as water, carbon dioxide and heptene.

30 The USD is designed so that sulfur-containing compounds are contained in the air stream which is required to support combustion when mixed with a second stream containing hydrogen gas. The optimum gas flow rates were determined to be 400 to 500 mL/min of air and
35 300 mL/min of hydrogen. Th optimum int rnal diameter

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for the quartz sampling probe was reported as about 0.1 mm. A key feature of the system reported by Benner and Stedman was the need to add a halogenated compound, such as CF_3Cl , into the air stream in order to achieve stable instrument baseline and long term instrument stability. The fundamental design of the USD precludes the measurement of non-sulfur containing compounds by conventional means such as the detection of ionic species produced in the flame.

In U.S. Patent No. 5,227,135, of which the present application is a continuation-in-part, there is described a process and apparatus for the simultaneous measurement of sulfur-containing compounds and non-sulfur-containing compounds based on the combustion of species in the hydrogen/air flame of a flame ionization detector, measurement of the ionic species produced in the flame, and concurrent withdrawal of sulfur monoxide produced in the flame and measurement of the sulfur monoxide by ozone-induced chemiluminescence.

The integrated detection system simultaneously measures organic compounds capable of producing ionic species upon combustion in the hydrogen/air flame and selectively measures all sulfur-containing compounds based on conversion of these sulfur-containing compounds in the same hydrogen/air flame to form sulfur monoxide, which is withdrawn from the flame and detected by means of ozone-induced chemiluminescence.

An important advantage of the integrated detector device is that it is not necessary to split the sample stream before it enters the detector cell. The selective detection system simultaneously forms both sulfur monoxide, from which sulfur-containing species are measured, and ions containing carbon, from which organic compound concentrations can be deduced. This device provides a means for direct operation of a "universal"

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detector (such as the flame ionization detector) and selective detection, without the need for splitting the sample stream. In addition, the response of two different detectors for the same compound is simultaneously measured, which greatly simplifies use of relative response factors in the identification of chemical compounds.

A difficulty with an instrument in which the flame used for a flame ionization detector is the same flame used to oxidize sulfur to produce sulfur monoxide, is that the optimal operating parameters for the flame ionization detector may not match the optimal operating parameters for oxidizing sulfur to produce sulfur monoxide. Therefore, while such a combination is feasible, it may not result in the best possible efficiency or sensitivity. Therefore, it is desirable to develop a system having the advantages of simultaneous detection of sulfur and non-sulfur compounds, but in a manner which allows the respective detection devices to be operated at optimal conditions for each.

SUMMARY OF THE INVENTION

The present invention includes a sulfur chemiluminescent detector and an interface with a flame ionization detector (FID), flame photometric detector (FPD) or other detector, for the purpose of simultaneously detecting sulfur compounds and non-sulfur compounds. In one embodiment, an externally heated transfer line is used to sample gases from the first detector which is used to detect non-sulfur compounds, and to transfer those gases to a burner to produce sulfur monoxide. In another embodiment, the burner is situated on top of the first detector, and gases from the first detector are sampled through a restrictor tube which is heated by thermal conduction and convection from a burner

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in the first detector such as the flame of a flame ionization detector or flame photometric detector.

5 In both embodiments, the probe used to sample gases from the first detector need not be inserted directly into the flame of the flame ionization detector or flame photometric detector. Instead, the probe can be positioned in a cooler zone of that detector. Positioning the probe in a cooler zone of the first detector also allows the probe to be constructed of materials other than aluminum oxide ceramics, such as fused silica, quartz or stainless steel. This also allows the FID, FPD or other detector that is used to detect non-sulfur compounds to be operated under conditions that are optimal for its performance without any effect from the probe. Surprisingly, the performance of the sulfur detector is not adversely affected by column bleed when operated in this manner.

BRIEF DESCRIPTION OF DRAWINGS

20 FIG. 1 is a schematic diagram of a preferred embodiment of the detector apparatus constructed in accordance with the present invention.

FIG. 2 is a schematic diagram of another preferred of the detector apparatus constructed in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

There is shown in FIG. 1 a preferred embodiment of the apparatus for the simultaneous detection of sulfur-containing compounds and non-sulfur-containing compounds after elution from a chromatographic column. The column 10 is contained in an oven 12, has an injection port 14 for injection of the sample and a supply 16 of the chromatographic mobile phase consisting of either a gas, liquid or supercritical fluid source.

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The effluent of the chromatographic column 10 is directed into the inlet of an apparatus 19 for the combustion of the chemical constituents of the carrier stream in a hydrogen/air flame. A commonly available flame ionization detector may be used such as a Hewlett Packard Model 5890, if adapted as described below. The hydrogen gas source 17 and a compressed air or oxygen source 15 is in fluid communication with the interior of combustion apparatus 19. Standard means for adjusting the flow of these gases to create an appropriate flame may also be included and are well known in the art. In the FID, an external electrical potential is applied between the base of the flame and a metal tube, which serves as a collector for ionic species formed in the flame. The existence and quantity of ionic species formed in the flame, are derived from the current generated between the base of the flame and the metal tube. The current data is transferred to a microprocessor unit 131, which is capable of displaying the current detected as a function of time on a recorder 33.

In conjunction with the measurement of ionic species formed in the flame, a flame sampling probe 28 is positioned in the FID to withdraw a portion of the flame gases from the flame assembly via a transfer line 30 into a burner 20. The burner 20 may be, for example, the Sievers Model 355 available from Sievers Instruments, Inc., Boulder, Colorado. Air is added to the burner to support combustion.

In the chemical reaction cell 36, the flame gases are mixed with a stream containing ozone produced by means of an electrical discharge of air or oxygen. Sulfur monoxide and other reactive species formed in the burner 20 will be carried to the chemical reaction cell 36 via the transfer line 31, and will undergo chemical reactions with ozone to produce species such as sulfur

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dioxide in an excited electronic state, which will emit radiation.

5 The transfer line 30 may be electrically heated tubing about 18 inches long with an inside diameter of .25 mm, which collects about 8 to 10% of the gases from the FID. The transfer line 30 may be of fused silica material.

10 The radiation emitted by the transient excited species is measured by means of a photomultiplier tube 38 after passage through an optical filter 42. A vacuum pump 44 is used to withdraw the gases from the flame via the sampling probe 28, the transfer line 31 into the chemical reaction cell 36, and withdraw the gaseous products after completion of the chemiluminescent
15 reaction from the reaction cell 36. A chemical trap 46 is used prior to the vacuum pump 44 to remove reactive chemical compounds, such as ozone and oxides of nitrogen, to prevent degradation of the vacuum pump and pump oil. A gas ballast and an oil return filter 48 is connected to
20 the exhaust of the vacuum pump to facilitate the removal of water vapor and other gases from the vacuum pump 44 and the recycling of oil vapor from the pump exhaust. The pump 44 is exhausted out vent 50.

25 The present invention is distinctly different from the USD system of Benner and Stedman discussed above. As previously noted, the design of the USD precluded the measurement of non-sulfur-containing compounds based on the formation of ionic species in the flame. In contrast with USD, in the present invention
30 the sample is mixed with a hydrogen stream and then is mixed with air and the temperature of the hydrogen/air flame 20 is much higher ($>1500^{\circ}\text{C}$) due to the higher gas flow rate employed and the use of a smaller size flame than the diffuse flame employed in the USD. The higher
35 flame temperatures are important in the formation of

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ionic species from organic compounds during combustion. Finally, the present invention does not require the addition of a halogen-containing compounds to the air stream for baseline stability.

5 The chemiluminescent reaction cell 36 is composed of aluminum and machined to an internal volume of about 10 cubic centimeters. There are four ports in the reaction cell 36. The transfer line 31 from the burner 20, enters through one port and into the interior of reaction cell 36. An ozone inlet tube enters through another port and into the interior of reaction cell 36. In a preferred embodiment, the ends of transfer-line 31 and the ozone inlet tube are within 10 millimeters.

10 The ozone inlet tube is in fluid communication with ozone generator 56. A source of compressed air or oxygen 60 is fed through conduit 62, via regulator 64 and filter 66, into ozone generator 56. Ozone generator 56 consists of an electrical discharge device that produces consistent and quantifiable amounts of ozone.

15 On the face of the chemical reaction cell 36, the optical filter 42 is held in a sealing relationship. All gases exit the reaction cell 36 via a third port. Light emitted by transient excited species within the interior of the reaction cell 36 passes through the optical filter 42, and is measured at the photomultiplier tube 38. Data concerning the quantity of light generated is transferred to controller 39 for display on recorder 41. The design of the chemical reaction cell is further described in U.S. Patent No. 5,227,135.

20 Another embodiment of the invention is shown in FIG. 2, wherein the burner 120 is positioned immediately above the FID so that the transfer line 130 can be heated by conduction and convection from the FID. In this embodiment, the transfer line 130 is only about 125 mm

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long and has an internal diameter of about one-sixteenth of an inch.

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CLAIMS

What is claimed is:

- 5 1. An apparatus for measuring sulfur and non-sulfur compounds in a sample, comprising a first detector to receive the sample, the first detector having a flame in a first detector chamber and capable of measuring non-sulfur compounds in the sample; a burner to produce sulfur monoxide; a heated transfer line with one end in communication with the first detector chamber and the
10 other end in communication with the burner to transfer the sample from the first detector chamber to the burner; an ozone reaction chamber for reacting said sulfur monoxide with ozone to produce excited state sulfur dioxide; and a chemiluminescent detector to detect
15 chemiluminescence of the excited state sulfur monoxide to measure sulfur.
2. The apparatus of claim 1, wherein the transfer line is heated electrically.
3. The apparatus of claim 2, wherein the
20 transfer line is between 12 and 24 inches long.
4. The apparatus of claim 3, wherein the transfer line has an internal diameter of approximately .25 inches.
5. The apparatus of claim 4, wherein the
25 transfer line collects 8 to 10% of the gases from the first detector chamber.
6. The apparatus of claim 1, wherein the burner is positioned above the first detector chamber and the transfer line has an inlet at a top of the first
30 detector chamber whereby the transfer line is heated by conduction and convection from the flame of the first detector chamber.
7. The apparatus of claim 6, wherein the transfer lin has a longitudinal axis that is
35 substantially vertical.

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8. The apparatus of claim 7, wherein the transfer line is less than 200 mm long.

9. The apparatus of claim 8, wherein the transfer line is approximately 125 mm long.

5 10. The apparatus of claim 7, wherein the transfer line has an internal diameter of approximately one-sixteenth inch.

10 11. A method of measuring sulfur and non-sulfur compounds in a sample, comprising: introducing the sample into a first detector chamber having a flame for the measurement of non-sulfur compounds; transferring gases produced in the first detector chamber to a burner via a heated transfer line; burning the transferred gases in the burner to produce sulfur monoxide; reacting the
15 sulfur monoxide with ozone to produce excited state sulfur dioxides and detecting the chemiluminescence of the excited state sulfur dioxide to measure sulfur.

20 12. The method of claim 11, wherein the step of transferring gases includes electrically heating the transfer line.

13. The method of claim 11, wherein the step of transferring the gases includes heating the transfer line by conduction and convection from the first detector chamber.

25 14. The method of claim 13, wherein said heating step includes positioning the burner above the first detector chamber so that the transfer line has a longitudinal axis that is substantially vertical.

30 15. The method of claim 14, wherein said heating step includes limiting the transfer line length to less than approximately 200 mm.

16. The method of claim 15, wherein said heating step includes limiting the transfer line internal diameter to approximately one-sixth inch.

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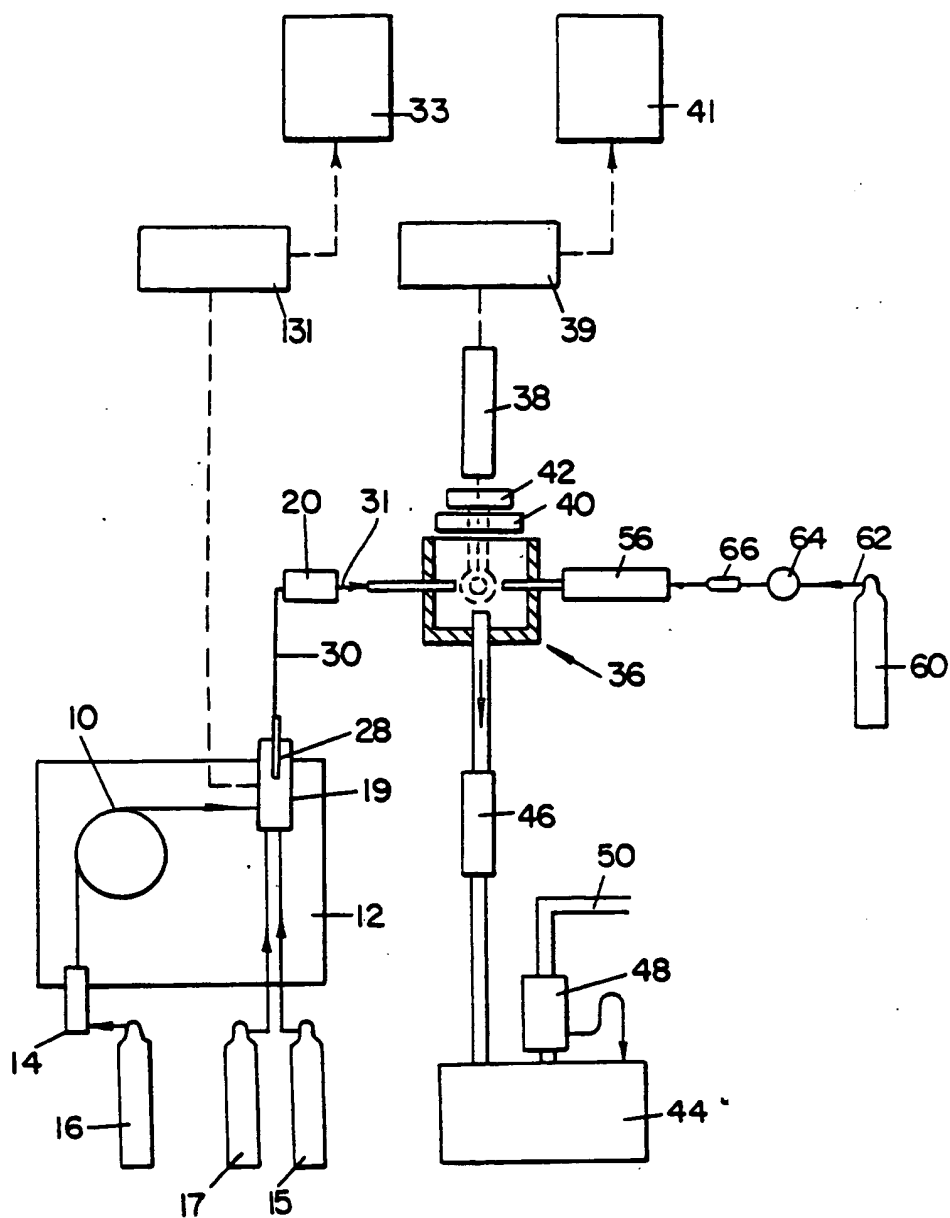


FIG. 1

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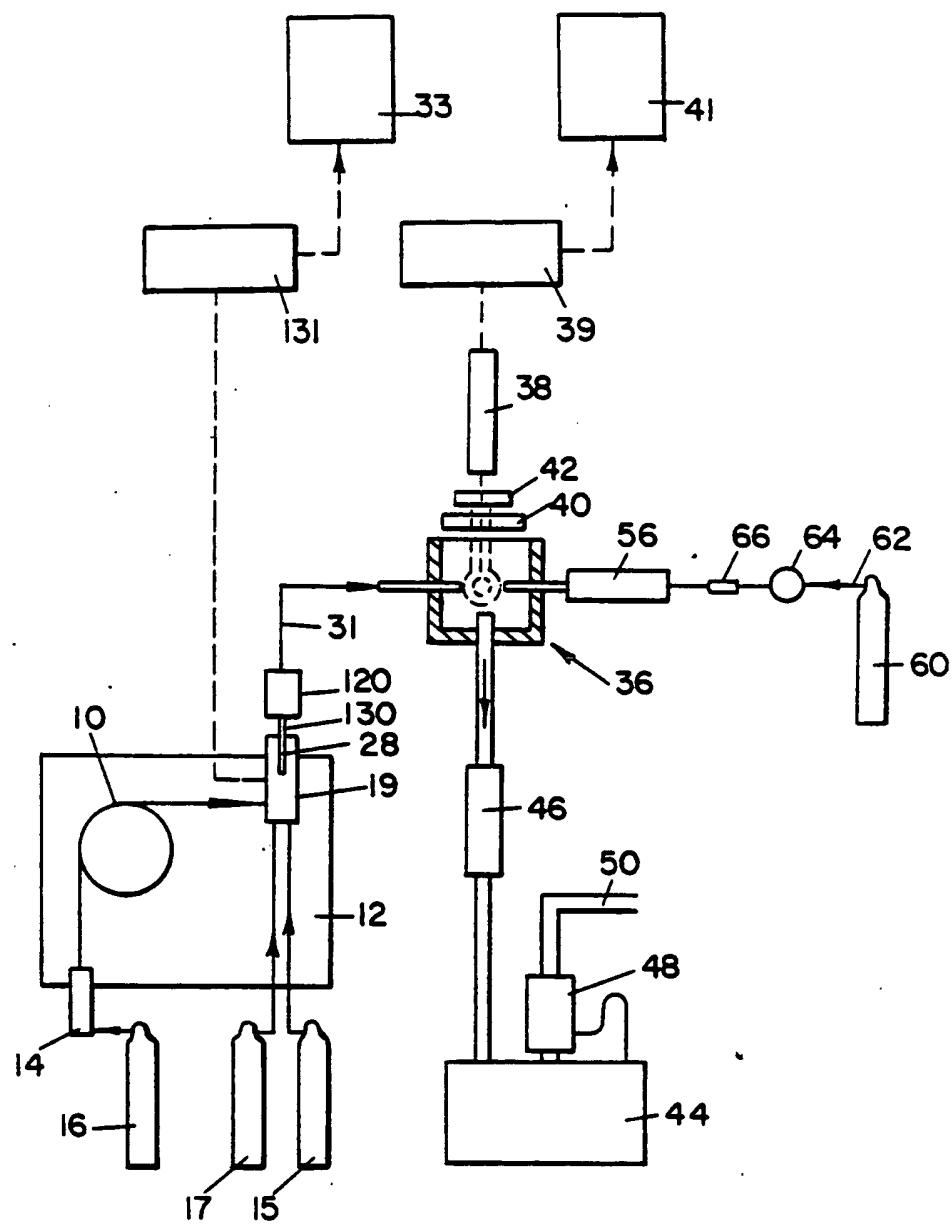


FIG. 2

INTERNATIONAL SEARCH REPORT

 International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(S) : G01N 21/76

US CL : 422/52.54; 436/122.123

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/52.54; 436/122.123

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,227,135 (GODEC ET AL.) 13 July 1993, see entire document.	1-16
Y	US, A, 4,111,554 (COLIN ET AL.) 05 September 1978, see entire document.	1-16
Y	Analytical Chemistry, Volume 61, No.11, issued 01- June 1989, Benner et al., "Universal Sulfur Detection by Chemiluminescence", pages 1268-1271, see entire document.	1-16
Y	Journal of Chromatography, Volume 347, issued 1985, Gaffney et al., "Gas Chromatographic Detection of Reduced Sulfur Compounds using Ozone Chemiluminescence", pages 121-127, see entire document.	1-16

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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INTERNATIONAL SEARCH REPORT**International application No.**
PCT/US95/01899**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,717,675 (SIEVERS ET AL) 05 January 1988, see entire document.	1-16